

## Flow-Injection Amperometric Determination of DOPA and Tyrosine at a Dual Electrode Modified with the Gold–Cobalt Binary System

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**Abstract**—The gold–cobalt binary system, electrodeposited on the surface of a screen-printed electrode, exhibits catalytic activity in the electrooxidation of DOPA and tyrosine. The catalytic effect is shown in a multiple increase in current compared with the oxidation current of the modifier and a decrease in the oxidation overvoltage of organic compounds. Methods for the flow-injection amperometric determination of DOPA and tyrosine at the proposed modified electrode are developed. The simultaneous amperometric determination of DOPA and tyrosine at a dual screen-printed electrode modified with an Au–Co binary system under the conditions of flow-injection analysis is demonstrated. The linear dependence of the analytical signal on the concentration of DOPA and tyrosine is observed in the ranges from  $1 \times 10^{-9}$  to  $1 \times 10^{-4}$  M and from  $5 \times 10^{-8}$  to  $5 \times 10^{-4}$  M, respectively.

**Keywords:** chemically modified electrodes, gold–cobalt binary system, dual screen-printed electrode, electrooxidation of DOPA and tyrosine, flow-injection analysis

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Automation of analytical works enables the rapid analysis of a large number of medicine, pharmaceutical, and environmental samples [1–3]. The use of flow methods, in which manual routine sample preparation procedures are replaced by simple automated operations of combining and mixing flows of the sample and reagent solutions, contributes to an increase in the productivity of chemical analysis [1]. To date, flow-injection analysis (FIA) using various detectors: mass spectrometric, optical, electrochemical, etc., is the most common in the laboratory practice. Among electrochemical detectors, amperometric ones are most often used [3–5], having a number of advantages like a wide linear dynamic range, high sensitivity, excellent reproducibility, and low cost of equipment.

FIA was widely spread in the analysis of biological fluids (blood plasma or serum, urine) [1, 6]. A large number of publications are devoted to the development of highly sensitive and selective amperometric methods for the detection of diagnostically important markers of diseases, for example, catecholamines [7, 8], purine bases [9], ascorbic acid [10], hemoglobin [11], insulin [12], glucose [13], etc., in a fluid flow. Chemically modified electrodes (CMEs) [7–13] are mainly used for amperometric detection; they enable reaching low detection limits and improve the selectivity of the determination of organic compounds. Various micro- and nanomaterials [7–13] are used as modifiers, including noble metals and bimetallic sys-

tems based on them [14–18], since in some cases, the latter have higher catalytic activity than individual metals [19, 20]. To reduce the cost of CMEs, it is advisable to use transition elements as a second metal.

The determination of DOPA and tyrosine (Tyr) is an important task in clinical diagnosis. DOPA (3-hydroxy-L-tyrosine) is a representative of catecholamines and the main precursor of dopamine biosynthesis. This compound is metabolized into dopamine by an enzymatic reaction, compensating for its deficiency in the brain, and is the main drug for the treatment of Parkinson's disease [21, 22]. Tyrosine (2-amino-3-(4-hydroxyphenyl)propanoic acid) is one of the most important aromatic amino acids. Tyrosine is responsible for the structure of most proteins in the human body, providing a positive nitrogen balance. In addition, this amino acid serves as a precursor for the synthesis of molecules of neurotransmitters such as dopamine, thyroxine, adrenaline, and melanin [23]. The Tyr metabolism disorder is found in diseases of liver and kidneys, alcoholism, as well as in hereditary pathology (tyrosinosis, alkaponuria, albinism) [23]. The concentration ratio of DOPA and Tyr is a specific marker of melanoma development [24].

In this paper, the catalytic activity of an Au–Co binary system electrodeposited on screen-printed electrodes with one or two working electrodes in the electrochemical oxidation of DOPA and Tyr is studied, and the possibility of using the catalytic response